

Effect of Overall Grafting Density on Microphase Separation of Mixed Homopolymer Brushes Synthesized from Y-Initiator-Functionalized Silica Particles

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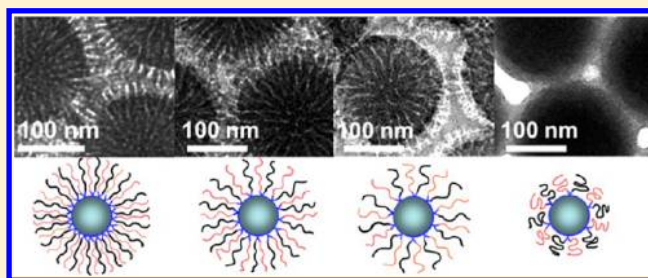
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S Supporting Information

ABSTRACT: We report in this article a systematic study on the effect of overall grafting density (σ_{overall}) on microphase separation of mixed poly(*tert*-butyl acrylate) (PtBA)/polystyrene (PS) brushes synthesized from asymmetric difunctional initiator (Y-initiator)-functionalized silica particles. The initiator particles were made by the immobilization of a triethoxysilane-terminated Y-initiator on the surface of 173 nm silica particles via an ammonia-catalyzed hydrolysis/condensation process in ethanol. Mixed PtBA/PS brushes were then grown from initiator particles by surface-initiated atom transfer radical polymerization of *t*BA at 75 °C and nitroxide-mediated radical polymerization of styrene at 120 °C. By changing the mass ratio of Y-initiator to silica particles in the initiator immobilization step, we found that the overall grafting density of mixed brushes can be systematically tuned while the individual grafting densities of two polymers remained comparable. A series of mixed PtBA/PS brushes with molecular weights of ~ 23 kDa for both PtBA and PS and σ_{overall} from 1.06 to 0.122 chains/nm² were prepared. Their microphase separation behavior was studied by transmission electron microscopy after the samples were drop-cast from chloroform onto carbon-coated TEM grids, annealed with CHCl₃ vapor, and stained with RuO₄. CHCl₃ is a good solvent for both grafted polymers. When the σ_{overall} was 0.34 chains/nm² and above, the mixed PtBA/PS brushes underwent lateral microphase separation, forming “rippled” nanostructures. The ripple wavelength (D) increased with decreasing σ_{overall} ; the normalized D scaled with $\sigma_{\text{overall}}^{-0.47}$ in the σ_{overall} range of 1.06–0.54 chains/nm². With further decreasing the grafting density, the phase separation became weaker, and no microphase separation was observed in the sample with σ_{overall} of 0.122 chain/nm².



INTRODUCTION

Binary mixed homopolymer brushes are composed of two chemically distinct homopolymers randomly or alternately immobilized by one end on a solid substrate.^{1–3} These brushes are an intriguing class of environmentally responsive nanostructured materials and have received tremendous interest in both fundamental and application studies in the past years.^{1–15} Marko and Witten were the first to investigate whether symmetric mixed homopolymer brushes on a flat substrate phase separate laterally forming a “rippled” nanostructure or vertically yielding a “layered” structure under equilibrium melt conditions.¹ They predicted that the lateral microphase separation preempted vertical microphase segregation, and the “rippled” nanostructure should be the one to appear. Since this seminal work, the lateral phase separation of mixed brushes under melt or near melt conditions and in nonselective or nearly nonselective solvents was repeatedly observed by many researchers in theoretical and simulation studies.^{2,4–8} In addition, the two grafted polymers in the brush layer can undergo spontaneous chain reorganization in response to

environmental changes, making mixed brushes exhibit different morphologies under different conditions. Because the polymer chains are covalently end-grafted on the substrate, the different nanostructures formed from the same mixed brushes are fully reversible. Since Sidorenko et al. reported the first synthesis of mixed brushes,⁹ the responsive properties of mixed homopolymer brushes have been extensively investigated,^{10–12} and the mixed brush-based “smart” materials have shown promise in many applications.

We have been particularly interested in the fundamental understanding of how various parameters, e.g., chain length disparity and grafting densities of two polymers, affect the phase behavior and responsive properties of mixed brushes.^{3,12,14,15} The effects of overall grafting density and relative grafting densities of two tethered polymers on phase morphology of mixed brushes have been theoretically

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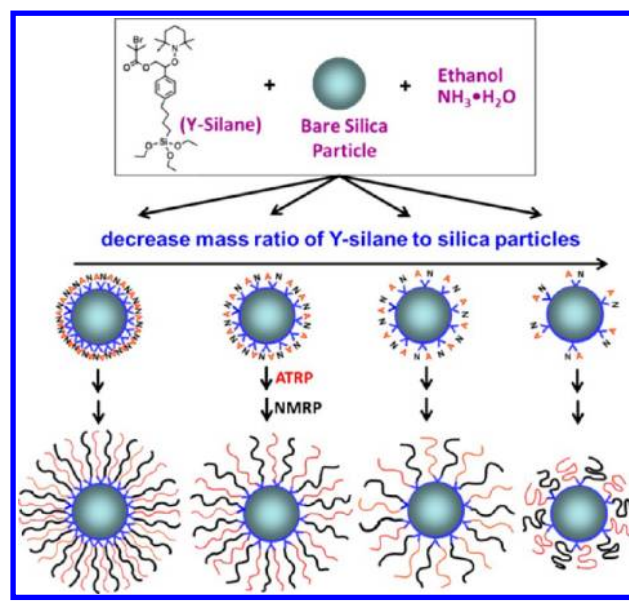
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investigated.^{4,6–8} In general, decreasing the grafting density leads to the weakening of the demixing interaction between two polymers in the brush layer.⁴ Because the grafting density determines the degree of stretching of polymer chains in the brush layer, it can be imagined that if the grafting densities are too low, the entropy loss due to the associated stretching in the phase segregation may not be compensated by the energy gain. In the limit where the two polymers are highly incompatible and their grafting densities are high, Zhulina and Balazs found, by scaling arguments, that in nonselective poor solvents the periodicity of the ripple pattern scales with the one-sixth power of the area per chain;⁴ i.e., the ripple wavelength decreases with the increase of overall grafting density. Relative grafting densities of two polymers in the brush layer also have a profound effect on the phase structures of mixed brushes, which have been revealed in a number of computer simulation studies.^{6–8} For instance, Wang and Müller observed that the morphology of mixed brushes on a flat substrate evolves from isolated domains of polymer A in a matrix of polymer B to rippled nanostructures to isolated domains of B in a matrix of A with the increase of the ratio of individual grafting densities of A to B.⁶ Roan and we studied the effect of relative grafting densities on the phase morphology of mixed brushes grafted on nanospheres and found that the morphology of mixed brushes varies from layered to various ordered polyhedral and rippled nanostructures with the change of relative grafting densities of two polymers.^{7,8}

To date, there has been no systematic experimental study on the effect of overall grafting density on phase morphology of mixed brushes, largely because of the challenge in the tuning of overall grafting density of mixed brushes while keeping individual grafting densities of two polymers similar. We recently reported the synthesis of a set of high grafting density mixed poly(*tert*-butyl acrylate) (PtBA)/polystyrene (PS) brushes with a fixed PtBA M_n of 18.6 kDa and PS M_n varying from 8.7 to 28.0 kDa on silica particles by sequential atom transfer radical polymerization (ATRP) of *t*BA and nitroxide-mediated radical polymerization (NMRP) of styrene and the morphological evolution of these mixed brushes with the change of chain length disparity of two grafted polymers.^{15b} The silica particles were functionalized with a triethoxysilane-terminated asymmetric difunctional initiator (Y-initiator) via an ammonia-catalyzed hydrolysis/condensation process. The overall grafting densities (σ_{overall}) of the obtained mixed brushes were in the range 0.9–1.2 chains/nm². Transmission electron microscopy (TEM) studies showed that the feature sizes of the nanopatterns formed from lateral microphase separation of mixed brushes were significantly smaller than those formed from intermediate grafting density mixed PtBA/PS brushes ($\sigma_{\text{overall}} = \sim 0.6$ chains/nm²) prepared from silica particles that were surface modified with a monochlorosilane-terminated Y-initiator.^{15a}

The work presented in this article was inspired by the theoretical prediction of Zhulina and Balazs⁴ and the aforementioned observations reported in the previous publications;¹⁵ we sought to elucidate the effect of overall grafting density on the ripple wavelength of the nanopattern formed from lateral microphase separation of mixed brushes through a systematic study. By varying the mass ratio of a triethoxysilane-terminated Y-initiator to bare silica particles (Scheme 1) in the initiator immobilization step, we found that the overall grafting density of mixed brushes synthesized from initiator particles can be systematically tuned while the

Scheme 1. Synthesis of Mixed Homopolymer Brushes with Various Overall Grafting Densities by Changing the Mass Ratio of Y-initiator to Silica Particles in the Initiator Immobilization Step via an Ammonia-Catalyzed Hydrolysis/Condensation Process



individual grafting densities of two polymers remained comparable. Transmission electron microscopy was then employed to study the nanostructures after the mixed brush-grafted particles were cast onto carbon-coated TEM grids, annealed with CHCl₃ vapor, and stained with RuO₄ vapor. CHCl₃ is a good solvent for both PtBA and PS. The ripple wavelength (D) was found to gradually increase with the decrease of σ_{overall} , and a scaling relationship between D and σ_{overall} was obtained. In addition, when the grafting density was sufficiently low, no microphase separation was observed.

EXPERIMENTAL SECTION

Materials. Tetraethyl orthosilicate (98%), ammonium hydroxide (25% in water), triethoxysilane (95%), and 2,2,6,6-tetramethylpiperidinoxy (TEMPO) were purchased from Acros Organics and used as received. The platinum–divinyltetramethyldisiloxane complex in xylene (2.1–2.4% Pt concentration in xylene) was obtained from Gelest, Inc. 2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate (Y-silane precursor) was prepared according to a procedure described in a previous publication.^{12f} Styrene (99%, Aldrich) and *tert*-butyl acrylate (*t*-BA, 99%, Aldrich) were dried with CaH₂, distilled under reduced pressure, and passed through a basic alumina column to remove the inhibitor. The purified monomers were stored in solvent storage flasks in a refrigerator prior to use. CuBr (98%, Aldrich) was stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol and ethyl ether. The salt was then collected, dried under vacuum, and stored in a desiccator. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (99%, Aldrich) and ethyl 2-bromoisobutyrate were dried with calcium hydride, distilled under a reduced pressure, and stored in a desiccator. 1-Phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (STEMPO), an initiator for NMRP, was prepared by following a procedure from the literature.¹⁶ All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

General Characterization. Size exclusion chromatography (SEC) was carried out at ambient temperature using PL-GPC 20 (an integrated SEC system from Polymer Laboratories, Inc.) with a refractive index detector, one PLgel 5 μ m guard column (50 \times 7.5 mm), and two PLgel 5 μ m mixed-C columns (each 300 \times 7.5 mm,

Table 1. Characterization Data for a Series of Mixed PtBA/PS Brush-Grafted Particle Samples with Different Overall Grafting Densities and Reaction Conditions for the Preparation of Corresponding Y-Initiator-Functionalized Silica Particles

initiator particles	mass ratio (%) of Y-initiator to particles ^a	mixed brushes	$M_{n,SEC}$ and PDI of PtBA ^b	$M_{n,SEC}$ and PDI of PS ^b	σ_{PtBA} , σ_{PS} , and $\sigma_{overall}$ (chains/nm ²) ^c
Y-Particle-1 ^d	108.8	MB-1	18 600, 1.09	19 400, 1.14	0.63, 0.43, 1.06
Y-Particle-2	85.8	MB-2	23 600, 1.09	23 500, 1.17	0.63, 0.40, 1.03
Y-Particle-3	86.6	MB-3	25 200, 1.09	21 900, 1.14	0.45, 0.50, 0.95
Y-Particle-4	43.7	MB-4	22 900, 1.09	22 200, 1.16	0.36, 0.32, 0.68
Y-Particle-5	32.1	MB-5	21 300, 1.10	20 700, 1.25	0.31, 0.23, 0.54
Y-Particle-6	15.6	MB-6	23 000, 1.09	21 900, 1.14	0.14, 0.20, 0.34
Y-Particle-7	8.13	MB-7	22 100, 1.10	23 500, 1.15	0.10, 0.022, 0.122
NA ^e	NA	MB-8	24 500, 1.11	24 900, 1.17	0.36, 0.27, 0.63

^aThe mass ratio of Y-silane precursor to bare silica particles used in the preparation of corresponding Y-initiator-functionalized silica particles. ^bThe values of number-average molecular weight ($M_{n,SEC}$) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) using polystyrene standards for calibration. ^c σ_{PtBA} , σ_{PS} , and $\sigma_{overall}$ are PtBA grafting density, PS grafting density, and overall grafting density ($\sigma_{overall} = \sigma_{PtBA} + \sigma_{PS}$). The grafting densities were calculated by using TGA data and molecular weights of PtBA and PS. ^dThe synthesis of Y-Particle-1 and the corresponding mixed PtBA/PS brushes MB-1 was reported in a previous publication.^{15b} The average size of bare silica particles used to prepare Y-Particle-1 was 172 nm, essentially the same as bare particles for Y-Particle-2 to -7. ^eThe Y-initiator-functionalized 160 nm silica particles used to synthesize MB-8 were made by using a monochlorosilane-terminated Y-initiator.^{15a}

linear range of molecular weight from 200 to 2 000 000 according to Polymer Laboratories, Inc.). THF was used as the carrier solvent at a flow rate of 1.0 mL/min. Polystyrene standards (Polymer Laboratories, Inc.) were employed for calibration. The data were processed using Cirrus GPC/SEC software (Polymer Laboratories, Inc.). ¹H NMR spectra were recorded on a Varian Mercury 300 MHz NMR spectrometer. Thermogravimetric analysis (TGA) was performed in air at a heating rate of 20 °C/min from room temperature to 800 °C using TA Q-series Q50. The particle samples for TGA were dried at 45 °C in vacuum for at least 5 h.

Synthesis of Bare Silica Particles. Ammonium hydroxide (25% in water, 19.909 g) and tetraethyl orthosilicate (TEOS, 10.504 g) were each mixed with 10 mL of ethanol. The two solutions were then added into a 500 mL one-necked flask that contained 280 mL of ethanol under the stirring condition. The concentrations of NH₃, TEOS, and water in the solution were 0.43, 0.15, and 2.92 M, respectively. The mixture was stirred vigorously at room temperature for 5.5 h. The particles were isolated by centrifugation (Eppendorf 5804 centrifuge, 8000 rpm), redispersed in ethanol, and centrifuged again. This washing process was repeated with ethanol an additional two times, water two times, and ethanol again. The particles were dried with a stream of air flow (3.20 g). The average diameter of silica particles, measured by transmission electron microscopy, was 173 nm. The bare silica particles were used to prepare Y-initiator-functionalized silica particles.

Synthesis of Y-Initiator-Functionalized Silica Particles. The triethoxysilane-terminated Y-initiator (Y-silane, Scheme 1) was immobilized onto the surface of silica particles via a hydrolysis/condensation process. The following is the procedure for the preparation of Y-initiator-functionalized silica particles, Y-Particle-4 (Table 1), which were used for the synthesis of mixed PtBA/PS brush-grafted particles with an overall grafting density of 0.68 chains/nm² (MB-4). Other initiator particles were made by using the same procedure except different amounts of Y-initiator (i.e., different mass ratios of Y-initiator to bare silica particles).

2-[4-(But-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate (Y-silane precursor, 65.9 mg, 0.138 mmol) was added into a 25 mL two-necked flask and dried at room temperature in vacuum for 1 h. Triethoxysilane (1.8 mL, 9.8 mmol) was added by a disposable plastic syringe into the flask under the N₂ atmosphere, followed by the injection of Pt complex in xylene (50 μL) using a microsyringe. The mixture was stirred at 45 °C under the nitrogen atmosphere; the hydrosilylation reaction was monitored by ¹H NMR spectroscopy analysis. Once the reaction was complete, excess triethoxysilane was removed under high vacuum at 45 °C, and the product, Y-silane, was used directly in the next step for the preparation of Y-initiator-functionalized silica particles (Y-Particle-4).

Bare silica particles (0.151 g) were dispersed in ethanol (14.0 mL) by ultrasonication to form a homogeneous, stable dispersion. A solution of ammonium (25% in water, 1.098 g) in ethanol (5.2 mL) was added dropwise into the particle dispersion. After the mixture was stirred at 40 °C for 2 h, a solution of Y-silane freshly synthesized from 65.9 mg of Y-silane precursor in ethanol (3.0 mL) was added dropwise into the dispersion. After the reaction mixture was stirred at 40 °C for 19 h, the particles were isolated by centrifugation and redispersed in THF. This process was repeated for a total of five times. The obtained Y-initiator particles were then dried with a stream of N₂ flow and used for the preparation of mixed homopolymer brush-grafted silica particles (MB-4).

Synthesis of PtBA Brush-Grafted Silica Particles. The Y-initiator particles (Y-Particle-4, 51.8 mg) were added into a 25 mL two-necked flask and dried under high vacuum at 35 °C overnight. The initiator particles were then dispersed in anisole (3.5 mL) by ultrasonication to form a stable dispersion. CuBr (22.5 mg, 0.157 mmol), *tert*-butyl acrylate (tBA, 12.006 g, 93.7 mmol), *N,N,N',N',N'*-pentamethyldiethylenetriamine (27.5 mg, 0.157 mmol), and ethyl 2-bromoisobutyrate (EBiB, 30.1 mg, 0.154 mmol) were added into a 50 mL three-necked flask and stirred under a N₂ atmosphere. The particle dispersion was then transferred into the 50 mL flask using a syringe, and the mixture was degassed immediately by three freeze–pump–thaw cycles. The flask was then placed into a 75 °C oil bath, and the polymerization was monitored by SEC and ¹H NMR spectroscopy analysis. After 64 h, the flask was removed from the oil bath and opened to air. THF (~10 mL) was added into the flask to dilute the mixture. The particles were isolated by centrifugation, and the supernatant was passed through a column of neutral, activated aluminum oxide to remove the copper catalyst. The particles were redispersed in THF. The dispersion was left to stand still at ambient conditions overnight, and the green precipitate was removed. The PtBA brush-grafted silica particles were separated by centrifugation again. This washing process was repeated with THF five times, followed by drying of the hairy particles with a stream of air flow. The $M_{n,SEC}$ and polydispersity index (PDI) of the free PtBA formed from free initiator EBiB in the polymerization were 22.9 kDa and 1.09, respectively, determined from SEC using PS as standards.

Preparation of Mixed PtBA/PS Brush-Grafted Silica Particles from PtBA Brush-Grafted Silica Particles with PtBA $M_{n,SEC}$ of 22.9 kDa. The PtBA brush-grafted silica particles (PtBA $M_{n,SEC}$ = 22.9 kDa, 19.1 mg) were dispersed in anisole (10.0 mL) in a 25 mL two-necked flask using an ultrasonic water bath. The particle dispersion was then transferred into a 50 mL three-necked flask that contain free initiator 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (STEMPO, 49.1 mg, 0.188 mmol) and 2,2,6,6-tetramethylpiperidinoxy (TEMPO, 3.2 mg), followed by the addition of styrene (15.017 g, 144.2 mmol). After the mixture was degassed by three freeze–

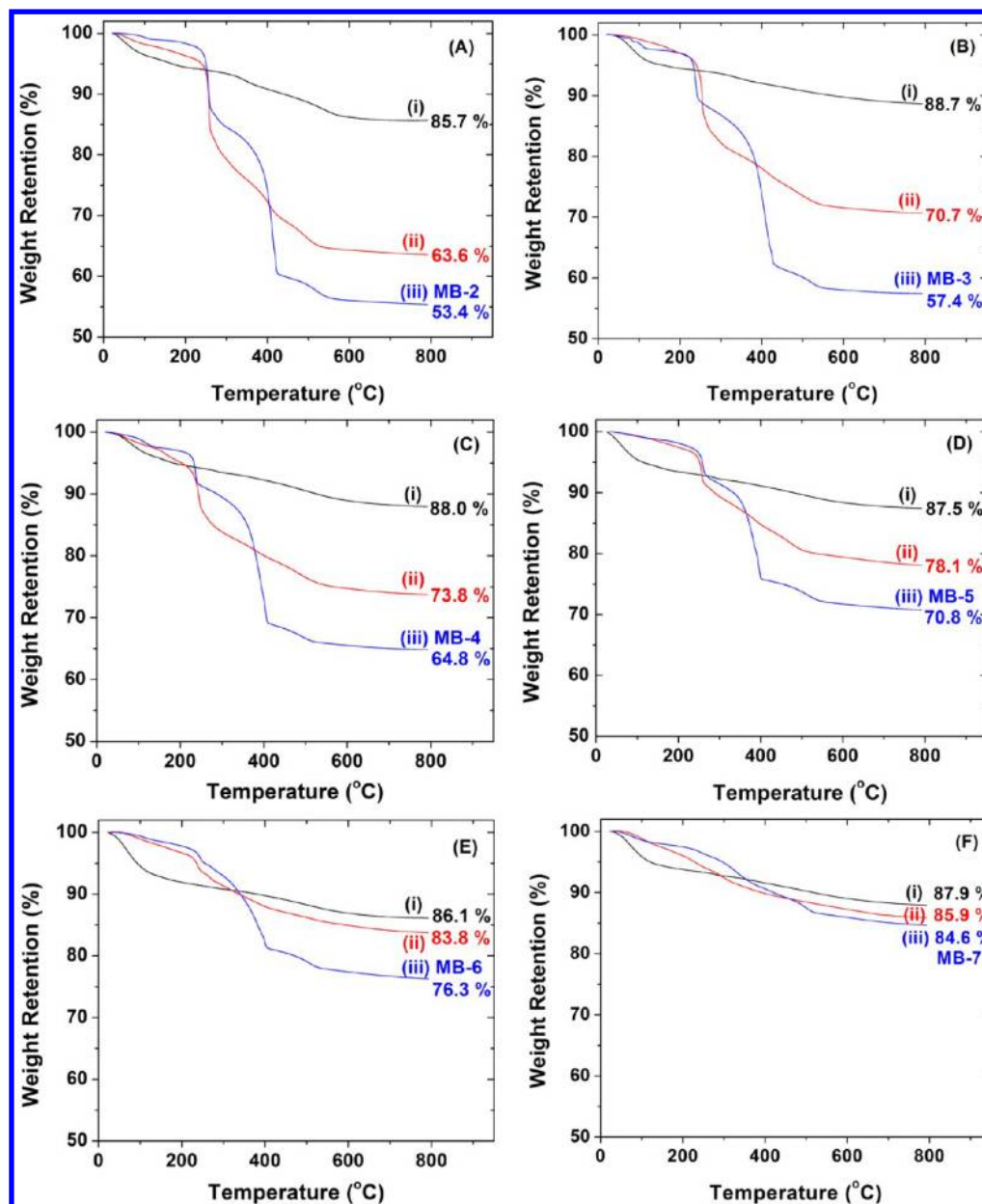


Figure 1. Thermogravimetric analysis (TGA) of (i) Y-initiator-functionalized silica particles, (ii) PtBA brush-grafted silica particles, and (iii) mixed PtBA/PS brush-grafted silica particles obtained in the preparation of mixed brush-grafted particle sample (A) MB-2, (B) MB-3, (C) MB-4, (D) MB-5, (E) MB-6, and (F) MB-7.

pump–thaw cycles, the flask was placed into a 120 °C oil bath. The polymerization was monitored by ^1H NMR spectroscopy and SEC. When the molecular weight of the free polystyrene reached the desired value, the polymerization was stopped by removing the flask from the oil bath and diluting the mixture with THF. The mixed PtBA/PS brush-grafted particles were isolated by centrifugation, redispersed in THF, and centrifuged again. This washing process was repeated four times to remove the physically adsorbed polymer. The particles were then dried with a stream of N_2 flow. The $M_{n,\text{SEC}}$ and PDI of the free polystyrene, measured by SEC, were 22.2 kDa and 1.16, respectively. Other mixed PtBA/PS brush-grafted silica particle samples and the corresponding PtBA brush-grafted silica particles were synthesized by using similar procedures.

Transmission Electron Microscopy (TEM) Study of Mixed PtBA/PS Brush-Grafted Silica Particles. Chloroform, a good solvent for both PtBA and PS, was used to prepare the particle dispersions. For each sample, ~ 1 mg of mixed PtBA/PS brush-grafted silica particles was dispersed in 1 mL of chloroform in a small vial by

ultrasonication in an ultrasonic water bath for 5 min. The particle dispersion was drop-cast onto a carbon-coated, copper TEM grid using a glass pipet and was allowed to dry at ambient conditions. The TEM samples were annealed with CHCl_3 vapor at room temperature as detailed below. The sample-loaded TEM grids were placed in a small glass dish with a diameter of 2 in. The dish was then transferred into a glass jar that contained ~ 2 mL of CHCl_3 . The jar was covered with a watch glass. After being annealed by CHCl_3 vapor at room temperature for at least 3 h, the samples were removed from the jar, allowed to dry at ambient conditions for 30 min, and then stained with RuO_4 at room temperature for 20 min. TEM experiments were performed on FEI Tecnai T12 at an accelerating voltage of 100 kV, and bright-field images were taken with a bottom-mounted Gatan CCD camera. The image analysis was performed using Nano Measurer 1.2 software.

RESULTS AND DISCUSSION

Synthesis of Mixed PtBA/PS Brushes with Various Overall Grafting Densities. To systematically study the effect of overall grafting density (σ_{overall}) on microphase separation of mixed brushes and to reveal the relation between σ_{overall} and ripple wavelength of the nanopattern, it is necessary to synthesize a series of mixed brushes with different overall grafting densities but similar molecular weights and comparable individual grafting densities for the two homopolymers. We previously reported the synthesis of high grafting density mixed PtBA/PS brushes ($\sigma_{\text{overall}} = 0.9\text{--}1.2$ chains/nm²) by using a triethoxysilane-terminated Y-initiator to functionalize silica particles.^{15b} This method of immobilizing the Y-initiator onto the surface of silica particles is similar to that reported by Ohno et al. for the fixation of an ATRP initiator.¹⁷ The key is the ammonia-catalyzed hydrolysis and condensation of the initiator-terminated triethoxysilane on the surface of bare silica particles in ethanol, yielding a high density initiator layer and hence high grafting density polymer brushes.

It is worth noting here that in the previous work a large amount of Y-initiator, 108.8 wt % with respect to silica particles with an average size of 172 nm, was used for the synthesis of high grafting density mixed PtBA/PS brushes.^{15b} We reasoned that by gradually changing the mass ratio of Y-initiator to silica particles with the same or a similar size in the initiator immobilization step, the Y-initiator density on the surface of silica particles would be different, which would lead to different overall grafting densities for mixed brushes. Therefore, we set out to make a series of Y-initiator particles from the same batch of bare silica particles with an average diameter of 173 nm by using different mass ratios of Y-initiator to silica particles. The other reaction conditions were kept identical. The bare silica particles were synthesized by the standard Stöber process, which is known to produce silica particles with a relatively uniform size distribution.¹⁸ The mass ratio of Y-silane precursor to bare silica particles ranged from ~86% to ~8% (Y-Particle-2 to -7, Table 1). The triethoxysilane-terminated Y-initiator was prepared by a platinum-catalyzed hydrosilylation reaction of 2-[4-(but-3-enyl)phenyl]-2-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethyl 2-bromo-2-methylpropanoate (the Y-silane precursor) with triethoxysilane (HSi(OC₂H₅)₃). For all initiator particles, the immobilization of Y-initiator onto the surface of silica particles was carried out at 40 °C for 19 h. The initiator particles were then isolated and repeatedly washed. For comparison, we also included in Table 1 the preparation of Y-initiator particles (Y-Particle-1) from 172 nm bare silica particles for the synthesis of high grafting density mixed brushes reported in a previous publication.^{15b}

The Y-initiator particles were then used to grow mixed PtBA/PS brushes with molecular weights of ~23 kDa for both polymers by following the established protocol from our laboratory.^{12f,15} PtBA was grown first by surface-initiated ATRP of *tert*-butyl acrylate in anisole at 75 °C using CuBr/*N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) as catalyst and ethyl 2-bromoisobutyrate (EBiB) as free initiator. The TEMPO group in the Y-initiator was previously confirmed to be stable under this ATRP condition.^{12f} The addition of a free initiator into the polymerization mixtures allowed the surface-initiated polymerizations to be controlled by the solution polymerizations. In addition, the polymerizations can be conveniently monitored by taking samples from the reaction mixtures. The polymerizations were stopped when the

molecular weights of the free PtBA reached the desired values. The PtBA brush-grafted silica particles were then repeatedly washed to remove the physically absorbed free polymer and characterized by thermogravimetric analysis (TGA).

Mixed PtBA/PS brushes were obtained by growing PS from PtBA brush-grafted silica particles via surface-initiated nitroxide-mediated polymerizations, which were carried out in anisole at 120 °C. Again, a free initiator, 1-phenyl-1-(2',2',6',6'-tetramethyl-1'-piperidinyloxy)ethane (STEMPO), was added into the reaction mixtures to facilitate the control of surface-initiated polymerizations. The mixed PtBA/PS brush-grafted silica particle samples were purified and analyzed by TGA to determine the polymer contents. Figure 1 shows the TGA data of six mixed PtBA/PS brush-grafted silica particle samples (MB-2 to -7 in Table 1) along with the corresponding Y-initiator particles and PtBA brush-grafted silica particles. It has been established that the molecular weight and molecular weight distribution of polymer brushes on silica particles synthesized by surface-initiated "living"/controlled radical polymerization, including high-density homopolymer brushes ($\sigma = 0.65\text{--}0.90$ chains/nm²) and mixed homopolymer brushes, are essentially identical to those of the free polymer formed from the free initiator.^{12f,17} By using the size of silica particles (173 nm), TGA data, and the molecular weights of PtBA and PS, and assuming that the density of silica particles was identical to that of bulk SiO₂ (2.07 g/cm³), the grafting densities of PtBA (σ_{PtBA}) and PS (σ_{PS}) on silica particles were calculated and are summarized in Table 1.¹⁹ The overall grafting density (σ_{overall}) for each sample, which is the sum of grafting densities of two polymers ($\sigma_{\text{PtBA}} + \sigma_{\text{PS}}$), is also included.

Figure 2 shows the plots of overall grafting density of mixed brushes σ_{overall} and individual grafting densities of PtBA and PS

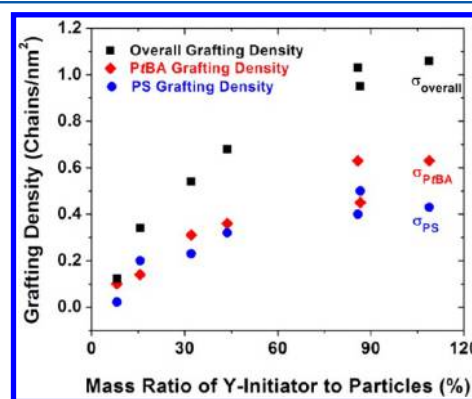


Figure 2. Plots of overall grafting density of mixed PtBA/PS brushes (σ_{overall} , black solid square), grafting density of PtBA (σ_{PtBA} , red solid diamond), and grafting density of PS (σ_{PS} , blue solid circle) on silica particles versus mass ratio of Y-initiator to silica particles used in the process of immobilizing the Y-initiator onto the surface of bare silica particles.

(σ_{PtBA} and σ_{PS}) versus mass ratio of Y-initiator to silica particles used in the preparation of Y-initiator-functionalized silica particles. Clearly, there is a correlation between σ_{overall} of mixed brushes and mass ratio of Y-initiator to silica particles; the higher the ratio, the higher the overall grafting density. From Table 1 and Figure 2, one can also find that the σ_{PtBA} and σ_{PS} are similar in most of mixed brush particle samples. For MB-1 and -2, σ_{PtBA} is larger than σ_{PS} by ~0.20 chains/nm², which could be due to the steric hindrance presented by the existing PtBA chains in the growth of PS chains. For the lowest

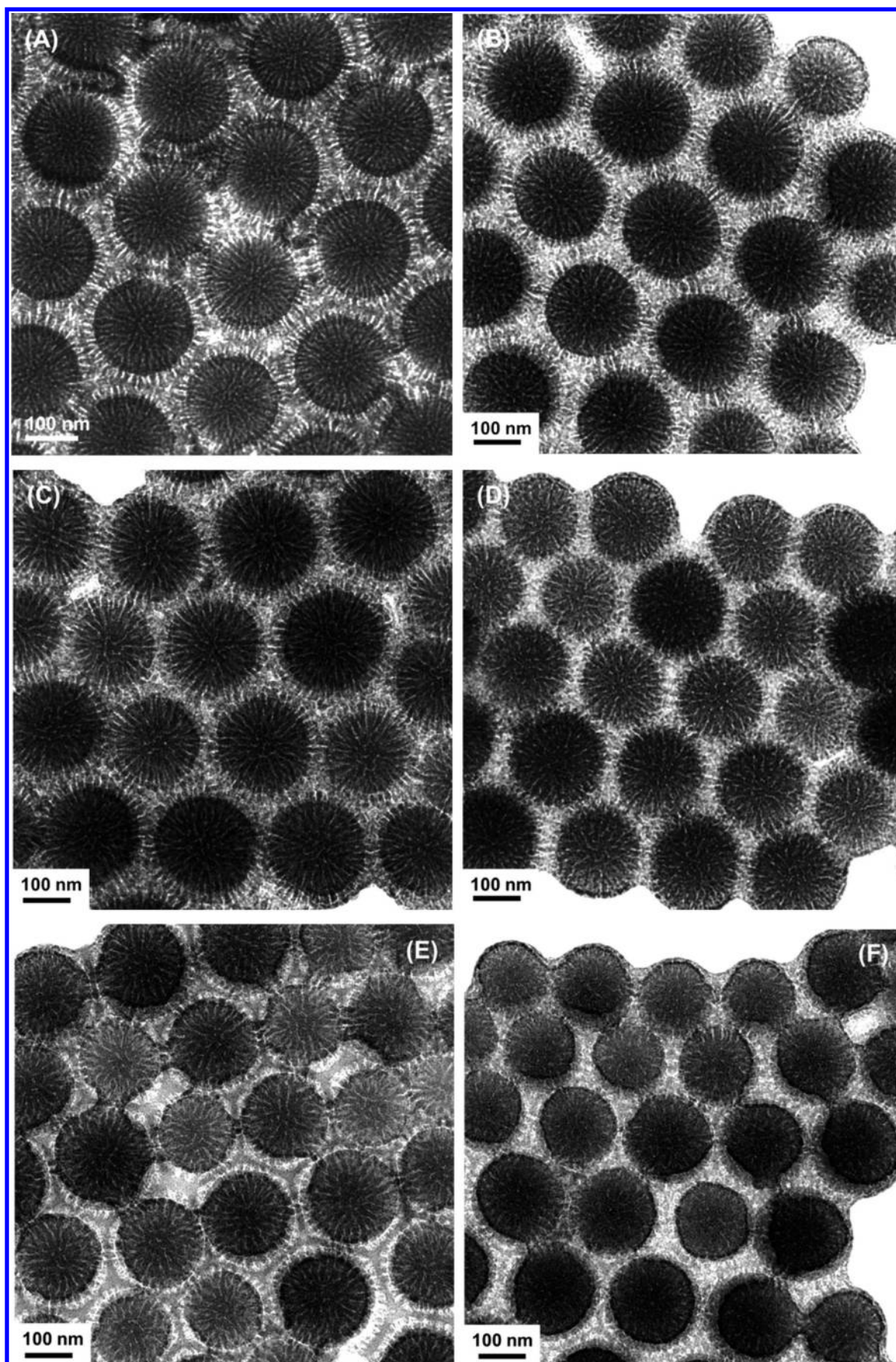


Figure 3. continued

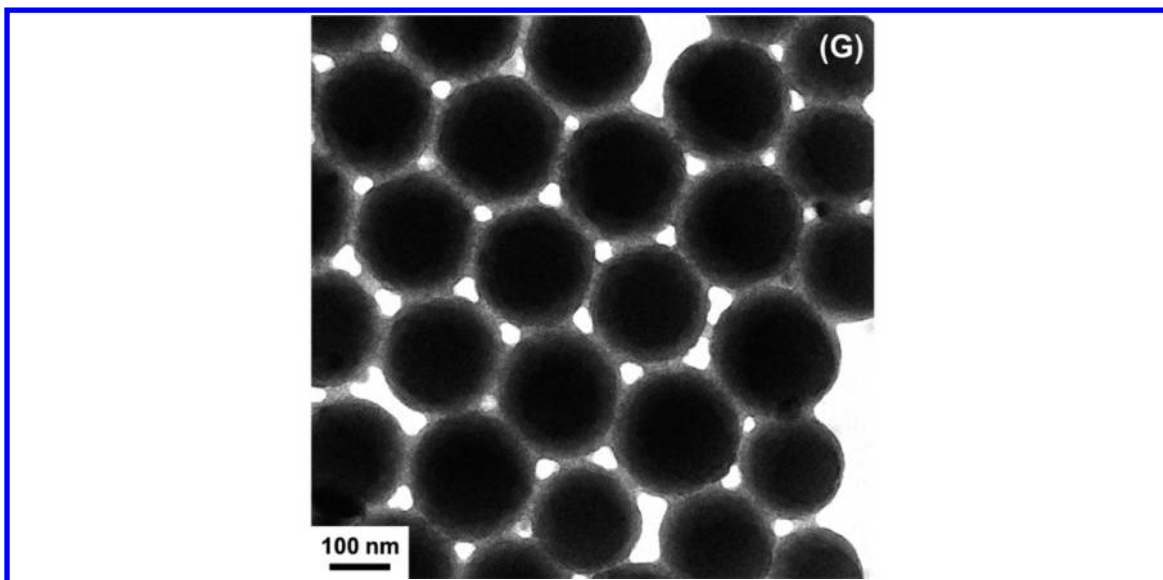


Figure 3. Top-view bright-field TEM micrographs of (A) MB-1 ($\sigma_{\text{overall}} = 1.06$ chains/nm²), (B) MB-2 ($\sigma_{\text{overall}} = 1.03$ chains/nm²), (C) MB-3 ($\sigma_{\text{overall}} = 0.95$ chains/nm²), (D) MB-4 ($\sigma_{\text{overall}} = 0.68$ chains/nm²), (E) MB-5 ($\sigma_{\text{overall}} = 0.54$ chains/nm²), (F) MB-6 ($\sigma_{\text{overall}} = 0.34$ chains/nm²), and (G) MB-7 ($\sigma_{\text{overall}} = 0.122$ chains/nm²) after being cast from CHCl₃ dispersions, annealed with CHCl₃ vapor for at least 3 h, and stained with RuO₄ vapor for 20 min.

overall grafting density sample (MB-7), the disparity between σ_{PtBA} (0.10 chains/nm²) and σ_{PS} (0.022 chains/nm²) may partly come from the inherent uncertainty in TGA analysis. We cleaved the grafted mixed PtBA/PS brushes from sample MB-7 by HF and collected the polymer mixture. ¹H NMR spectroscopy analysis showed that the molar ratio of PtBA to PS units was 100 to 64.3, which corresponded to the molar ratio of PtBA and PS chains of 100 to 54.5 (= ratio of grafting densities of PtBA and PS). If the overall grafting density is still 0.122 chains/nm², the individual grafting densities of PtBA and PS would be 0.079 and 0.043 chains/nm², respectively. Since our focus in this work is the effect of overall grafting density on ripple wavelength of the nanopattern formed from lateral microphase separation of mixed brushes, the small difference in the grafting densities of two polymers should not affect the ripple wavelength much because many simulation works have shown that the lateral microphase separation can tolerate small variations in grafting densities and molecular weights of two end-tethered homopolymers.⁶

TEM Study of Mixed PtBA/PS Brushes with Various Overall Grafting Densities. For TEM study of microphase separation, mixed PtBA/PS brush-grafted silica particle samples were dispersed in CHCl₃, a good solvent for both PtBA and PS, and drop-cast onto carbon-coated TEM copper grids. The TEM samples were then annealed with CHCl₃ vapor in a closed container for at least 3 h and stained with RuO₄ vapor at room temperature for 20 min. Note that RuO₄ vapor selectively stains PS, making PS and PtBA nanodomains appear dark and bright, respectively, under TEM.¹⁴ We previously showed that without staining with RuO₄ the nanostructures formed from microphase separation of mixed PtBA/PS brushes cannot be seen.^{14a}

Figure 3 shows representative top-view bright field TEM micrographs of six mixed PtBA/PS brush samples (MB-2 to -7) and a TEM image of MB-1 from a previous publication,^{20,15b} which are arranged in the order of decreasing the overall grafting density of mixed brushes. Clearly, in samples of MB-2 to -5, mixed PtBA/PS brushes were microphase separated,

forming rippled nanostructures composed of dark PS and bright PtBA nanostripes. This is consistent with our previous observations that nearly symmetric mixed brushes underwent lateral microphase separation¹⁵ and also with the results from computer simulations.⁶ By looking through the TEM micrographs in Figure 3, one can easily recognize that the feature size gradually increases with the decrease of overall grafting density, which is qualitatively in agreement with the prediction of Zhulina and Balazs.⁴ The nanopatterns formed by MB-2 and -3 (Figure 3B,C) are similar to that of MB-1, the sample that has the highest overall grafting density. On the other hand, the feature size of MB-5 with σ_{overall} of 0.54 chains/nm² in Figure 3E is apparently larger with a typical ripple wavelength of ~19 nm. This is very similar to the nanopattern formed by intermediate grafting density mixed PtBA/PS brushes on 160 nm silica particles ($\sigma_{\text{overall}} = \sim 0.60$ chains/nm²) that we reported before.^{15a} Thus, these new results corroborate our previous observations on the lateral microphase separation of high and intermediate grafting density mixed PtBA/PS brushes.¹⁵

Although in MB-6 dark and bright domains are still discernible (Figure 3F), the nanopattern is not as clear as in MB-5 (Figure 3E); the driving force for phase separation in MB-6 appears to become weaker. Interestingly, while the polymer brushes can be clearly seen between neighboring particles and in the interstitial spaces among particles, no microphase separated nanostructures are observed in MB-7 (Figure 3G); the two grafted polymers were in the miscible state. We believe that the low σ_{overall} and the fluctuation of grafting sites should be responsible for these observations. With the decrease of σ_{overall} to a certain degree, the microphase separation may become unfavorable because phase separation involves further stretching of polymer chains. The entropy loss associated with lateral phase separation is not compensated by the enthalpy gain. Consequently, the miscible state is the one having the lowest Gibbs free energy. This should be the case for MB-7.²¹ On the other hand, the increased fluctuation of grafting sites may also contribute to the weakened lateral

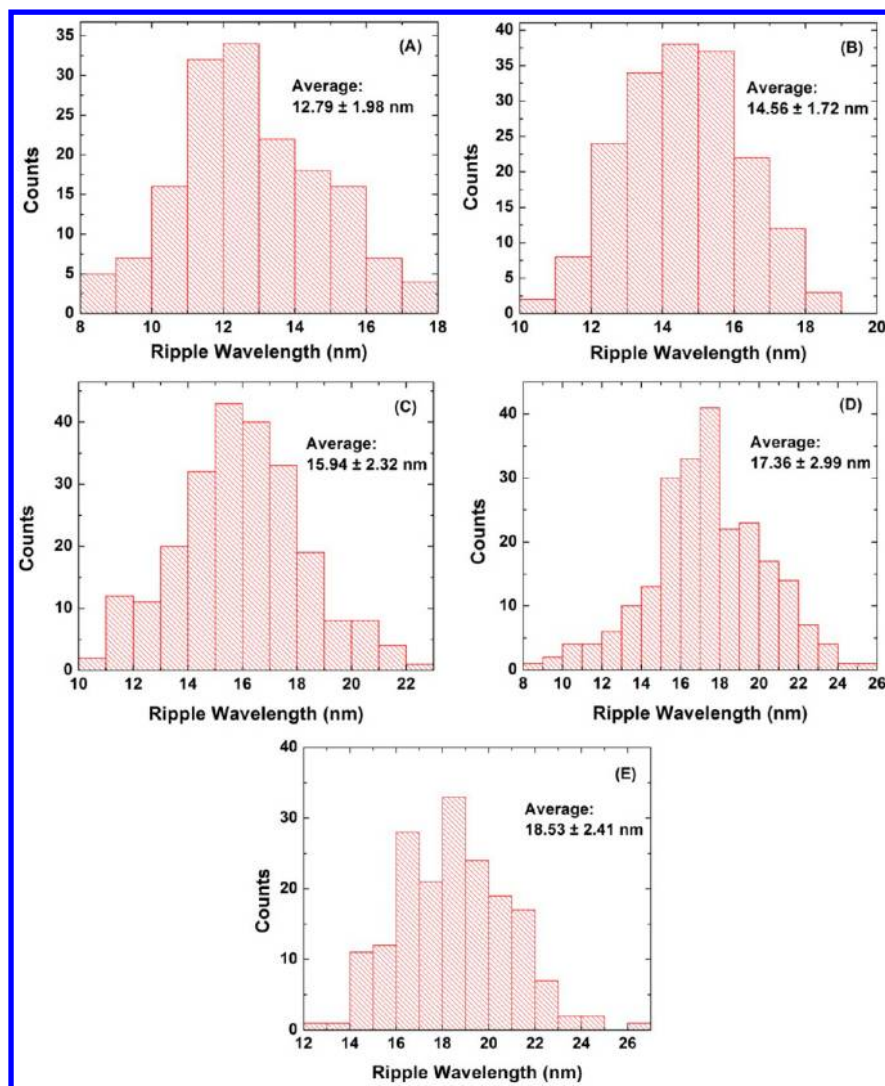


Figure 4. Distributions of ripple wavelengths of features (sum of widths of neighboring PtBA and PS stripes) obtained from TEM image analysis of (A) Figure 3A, MB-1, (B) Figure 3B, MB-2, (C) Figure 3C, MB-3, (D) Figure 3D, MB-4, and (E) Figure 3E, MB-5.

microphase separation of MB-6 and no phase segregation of MB-7. With the decrease of the amount of Y-initiator used in the preparation of Y-initiator-functionalized silica particles (only 15.6 and 8.13 wt % of Y-initiator were used for MB-6, and -7, respectively), the fluctuation of Y-initiator density on the surface of silica particles may not be negligible; i.e., the Y-initiator and thus the grafted PtBA and PS chains may not be uniformly distributed on the surface of particles. With the departure from the symmetric composition, a higher interaction strength is required for microphase separation, which can be seen from the phase diagram of diblock copolymers.²² The simulation work of Wenning et al. suggested that the density and composition fluctuations of grafting points enhance the formation of irregular nanostructures and prevent the appearance of long-range order.^{5e}

Using software Nano Measurer 1.2, we conducted image analysis of TEM micrographs A–E in Figure 3 by selecting the features in the area between the half radius ($R/2$) and the periphery (R) from the particle center (i.e., the edge view of the particles). As can be seen from Figure 3A–E, the features in this area tend to be clearer, which would make the analysis more accurate. The results are presented in Figure 4 as plots of counts versus ripple wavelength (sum of widths of neighboring

PtBA and PS stripes). As expected, the average ripple wavelength increases with the decrease of σ_{overall} , from 12.8 nm for MB-1, to 14.6 nm for MB-2, to 15.9 nm for MB-3, to 17.4 nm for MB-4, and 18.5 nm for MB-5.

The molecular weights of PtBA and PS in mixed brush samples MB-1 to -5 are not exactly the same. Theoretical studies have shown that the ripple wavelength of the nanopattern formed from lateral phase separation of mixed brushes is proportional to the square root of molecular weight.⁴ Therefore, to better compare the ripple wavelength and extract the scaling relationship between ripple wavelength and σ_{overall} , we normalized the average ripple wavelengths from TEM image analysis by using the molecular weights of PtBA and PS of mixed brushes MB-4 as reference. That is, normalized ripple wavelength = average ripple wavelength / $\{[(M_{n,\text{SEC-PtBA}} + M_{n,\text{SEC-PS}})/(M_{n,\text{SEC-PtBA-4}} + M_{n,\text{SEC-PS-4}})]^{1/2}\}$. The results are included in Table 2. To help obtain the relation between ripple wavelength and σ_{overall} , we also analyzed a TEM image of an intermediate grafting density mixed PtBA/PS brush sample (MB-8 in Table 1, the TEM picture is included in the Supporting Information) from a previous publication.^{15b} As can be seen from Table 2, the normalized average wavelength (D_N) also increased with the decrease of overall grafting density.

Table 2. Average Ripple Wavelengths of Nanopatterns Formed by Lateral Microphase Separation of MB-1 to -5 and MB-8 from TEM Image Analysis and Average Ripple Wavelengths Normalized Against the Molecular Weights of MB-4

mixed brushes	$M_{n,SEC}$ of PtBA	$M_{n,SEC}$ of PS	$\sigma_{overall}$ (chains/nm ²)	av ripple wavelength (D_N), ^a nm	normalized ripple wavelength (D_N), ^b nm
MB-1	18 600	19 400	1.06	12.8	13.9
MB-2	23 600	23 500	1.03	14.6	14.3
MB-3	25 200	21 900	0.95	15.9	15.6
MB-4	22 900	22 200	0.68	17.4	17.4
MB-5	21 300	20 700	0.54	18.5	19.2
MB-8 ^c	24 500	24 900	0.63	19.5	18.6

^aAverage ripple wavelength obtained from image analysis of TEM micrographs (Figure 4). ^bNormalized ripple wavelength = average ripple wavelength/ $\{[(M_{n,SEC-PtBA} + M_{n,SEC-PS})/(M_{n,SEC-PtBA-4} + M_{n,SEC-PS-4})]^{1/2}\}$. ^cMixed PtBA/PS brush-grafted silica particles (silica particle size = 160 nm) synthesized from silica particles functionalized by using a monochlorosilane-terminated Y-initiator (PtBA M_n = 24.5 kDa, PDI = 1.11, σ_{PtBA} = 0.36 chains/nm²; PS M_n = 24.9 kDa, PDI = 1.17, σ_{PS} = 0.27 chains/nm²).

Figure 5 shows the plot of D_N versus overall grafting density $\sigma_{overall}$ on a double-logarithmic scale. A linear dependence of log

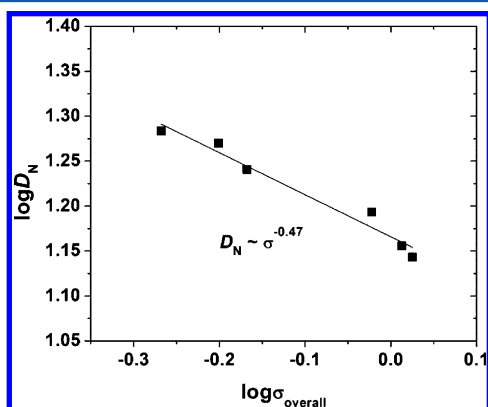


Figure 5. Plot of $\log D_N$ versus $\log \sigma_{overall}$, where D_N is the normalized ripple wavelength and $\sigma_{overall}$ is the overall grafting density of mixed brushes. The straight solid line is a linear fit with $R = 0.983$ and a slope of -0.47 .

D_N on $\log \sigma_{overall}$ with a slope of -0.47 was observed (linear fit $R = 0.983$), suggesting that in the range of overall grafting density of 0.54–1.06 chains/nm² the ripple wavelength scales with -0.47 power of overall grafting density, i.e., $D_N \sim \sigma_{overall}^{-0.47}$. This means that our experimentally observed D_N has a stronger dependence on $\sigma_{overall}$ than that predicted by Zhulina and Balazs ($D \sim \sigma_{overall}^{-1/6}$),⁴ though the general trend is the same. The experimentally observed ripple wavelength appears to be approximately proportional to the average distance between neighboring chains in the overall grafting density range of 0.54–1.06 chains/nm² for our system. The discrepancy observed here could arise from the different conditions used in our experiments and in the theoretical consideration. In our experiments, the mixed PtBA/PS brush-grafted particles were cast from a dispersion in CHCl₃, a good solvent for both polymers, and annealed with CHCl₃ vapor. In the theoretical study of Zhulina and Balazs,⁴ the scaling relationship was obtained from perfect symmetric mixed brushes in nonselective

poor solvents in the limit where the two polymers are highly incompatible, and their grafting densities are high. In addition, our samples are not perfect Y-shaped mixed brushes. Nevertheless, our experimental results have revealed the basic feature of how the ripple wavelength of the nanopattern formed from lateral microphase separation of mixed homopolymer brushes changes with $\sigma_{overall}$.

CONCLUSIONS

A systematic study on the effect of overall grafting density on microphase separation of mixed PtBA/PS brushes grafted on 173 nm silica particles was carried out. By varying the mass ratio of Y-initiator to bare silica particles in the initiator immobilization step, a series of mixed PtBA/PS brushes with different overall grafting densities but similar molecular weights and comparable individual grafting densities for the two polymers were obtained. The mixed brushes were grown by sequential ATRP of *t*BA and NMRP of styrene. TEM studies showed that the feature size of the nanopattern formed from lateral microphase separation increased with the decrease of overall grafting density. The normalized ripple wavelength was found to scale with $\sigma_{overall}^{-0.47}$ in the $\sigma_{overall}$ range of 0.54–1.06 chains/nm². When the grafting density was sufficiently low, no microphase separation was observed, presumably because at a sufficiently low grafting density the entropy loss from phase separation cannot be compensated by the enthalpy gain, resulting in the miscible state being favored. This is the first time that the effect of overall grafting density on lateral microphase separation of mixed homopolymer brushes was systematically investigated. The results could provide a guide for potential applications of mixed homopolymer brushes.

ASSOCIATED CONTENT

Supporting Information

Calculation of grafting densities of PtBA and PS on silica particles; more TEM micrographs of MB-1 to -7 after the samples were annealed with CHCl₃ vapor and stained with RuO₄ vapor; a TEM micrograph of MB-8 from a previous publication (reference 15b) and the image analysis result; synthesis and TEM study of two additional low overall grafting density mixed PtBA/PS brush samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (19) The molecular weights of PtBA measured by SEC against PS standards were used in the calculation of PtBA grafting densities. We previously observed that the PtBA molecular weights from SEC were very close to those calculated from the monomer-to-initiator ratio and monomer conversion. See refs 12f and 15. The difference between weight retentions of Y-initiator-functionalized particles and polymer brush-grafted silica particles at 100 °C is presumably caused by the water content, though all samples were dried under high vacuum at 45 °C for at least 5 h. This difference was taken into consideration in the calculation of grafting density of polymer brushes by vertically shifting the curves to the same position—the highest weight retention at 100 °C among three curves as described in ref 18b. The calculation of grafting densities of PtBA and PS in MB-5 is presented in the Supporting Information as an example.
- (20) More TEM micrographs can be found in the Supporting Information.
- (21) To further confirm that there is no microphase separation when the overall grafting density of mixed brushes is sufficiently low, we synthesized two additional samples using 181 nm silica particles. The molecular weights of polymers are similar (~21 kDa), and the overall grafting densities of two samples are 0.20 and 0.09 chains/nm². TEM studies showed no microphase separation. The details are included in the Supporting Information.
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